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Application of EPA Method 610 to the Analysis of Polynuclear Aromatic Hydrocarbons in Leachate Samples

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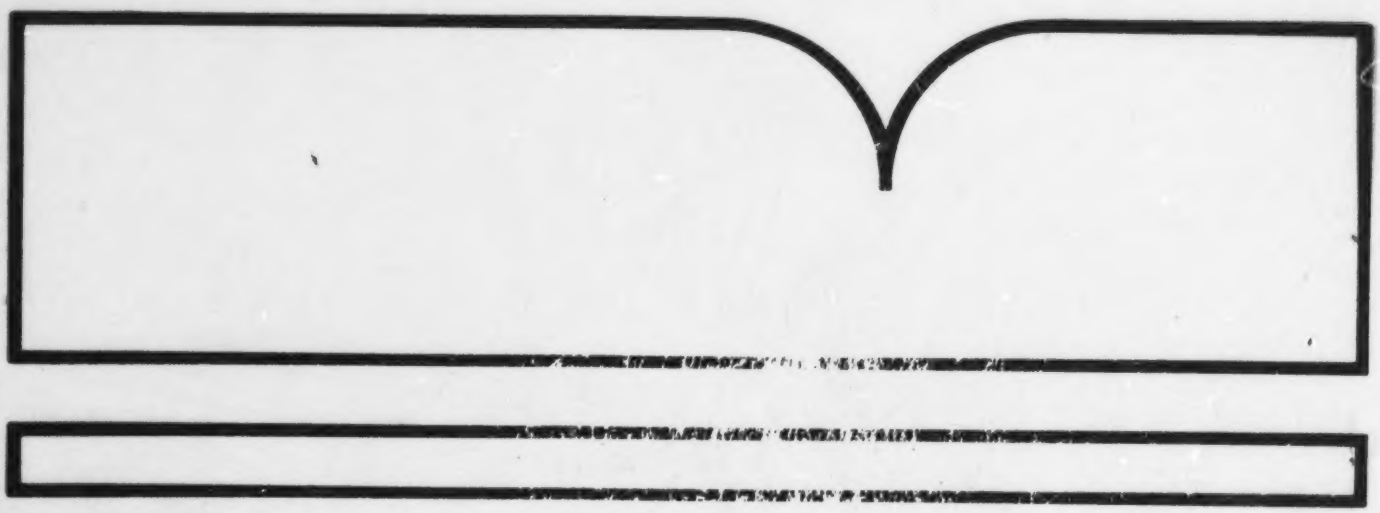
Cincinnati, OH

May 82



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APPLICATION OF EPA METHOD 610 TO THE ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS IN LEACHATE SAMPLES

by

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This report summarizes the results of a spiking study performed on a sanitary landfill leachate matrix. Fifteen polynuclear aromatic hydrocarbons (PNAs) were dosed into the landfill leachate and analyzed using EPA Method 610. The results show that the PNAs containing two, three, or four fused rings gave recoveries greater than 50%. Those PNAs containing five or six fused rings gave recoveries less than 50%. All PNAs were spiked at the low µg/L to the mid ng/L range.

The leachate matrix was also analyzed by gas chromatography/mass spectrometry (GS/MS) to identify the compounds present in this complex matrix. Forty-three compounds were given a tentative or confirmed identification after packed column and capillary column GC/MS analysis. There were an additional 65 compounds present in the leachate extract that could not be identified.

Further research needs to be performed to improve the accuracy for the analysis of high molecular weight PNAs in leachate samples.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report describes the application of EPA proposed Method 610 for the analysis of polynuclear aromatic hydrocarbons (PNA) in a sanitary landfill leachate. This report will be useful for identifying problem areas in the analysis of PNAs in leachate matrices.

Robert L. Booth

Robert L. Booth, Acting Director
Environmental Monitoring and Support
Laboratory - Cincinnati

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SECTION 1

INTRODUCTION

EPA Method 610, Polynuclear Aromatic Hydrocarbons, was designed for the analysis of 16 PNA compounds in municipal and industrial discharges. Samples of a leachate from a sanitary landfill were obtained and analyzed using Method 610 to determine if this method is applicable for the analysis of PNA compounds in a leachate matrix. Leachate samples were also spiked and analyzed to determine the precision and accuracy of Method 610 for a leachate matrix.

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SECTION 2

EXPERIMENTAL

One liter samples were extracted with methylene chloride, concentrated, and passed through a silica gel cleanup column as described in Method 610. The final extract volume was 1.0 mL. A 4.6 mm x 25 cm Zorbax LC column was used for HPLC analysis. Since resolution of benzo(a)anthracene and chrysene could not be achieved, only benzo(a)anthracene was used in subsequent work. The column conditions were isocratic 10 minutes at 70% acetonitrile in water, then a 20 minute linear program to 100% acetronitrile at a flow rate of 1.5 mL per minute. Naphthalene, acenaphthylene, acenapthene and flourene were quantitated using a UV detector set at 254 nm. The remaining PNAs were quantitated using a flurometer operated with excitation at 280 nm and reporting all emission greater than 389 nm. (Corning 3-75 filter or equivalent). Samples were spiked in the original container, stored overnight at 4°C, then extracted the following day.

Packed column gas chromatography mass spectrometry (GC/MS) was done using a 2m x 2mm glass column packed with 3% OV-17 on 100/120 mesh Gas Chrom Q. The temperature program was four minutes at 50°C then 5°C per minute to 300°C. Capillary column GC/MS was done using a 30 m x 0.25 mm fused silica column coated with SE-54. The temperature program was four minutes at 40°C then 10°C per minute to 275°C.

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SECTION 3

RESULTS

The leachate was collected in January and May of 1981 at a large sanitary landfill in Colerain Township, Hamilton County, Ohio. The site uses the area method of landfilling and presently deposits solid waste at a rate of 11.9 Gg per week. At the collection site, a horizontal 10 cm O.D. pipe is embedded 9 meters deep into the side of a hill that contains solid waste deposited since 1970. The leachate runs out of the pipe at a rate of 7.5 liters per minute and travels about 20 meters down a slope to a holding pond. The samples were collected at the end of the pipe before contact with the ground. This leachate represents all sources of water that have percolated through this 15 meter deep section of the landfill.

The leachate was straw colored, foamed, had a slightly disagreeable odor, and exhibited a pH of 7.6. Samples were collected in amber glass containers having Teflon-lined caps and were stored at 4°C protected from the light.

The leachate spiking study revealed a serious matrix effect for PNA compounds containing five or six fused rings. The results are summarized in Table 1 and demonstrate a trend for much lower recovery with an increasing number of fused rings.

Figure 1 displays the recovery as a function of the matrix type and number of fused rings. The high recoveries for A-naphthalene, D-fluorene, and G-fluoranthene are due to the relative magnitude of the amount spiked to the amount present in the background. In each of these three cases, the leachate was spiked at approximatey one third the background level. The remaining PNA compounds were spiked at a level at least twice the background level. All recoveries from reagent water are consistent and show no trend. The correlation coefficients for recovery versus number of fused rings are -0.867 for the leachate matrix and 0.414 for reagent water when the results for compounds A,D, and G are included and are -0.954 and 0.448 when these three compounds are not included.

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Examination of the HPLC chromatograms in Figure 2 - fluoresence detector and Figure 3 - UV detector, shows that the leachate extract, after silica gel column cleanup, is not exceptionally complex. The major peaks in the leachate background in Figure 2 correspond to A-naphthalene, 1- and 2-methyl naphthalene, C-acenaphthene, E-phenanthrene, G-fluoranthene, H-pyrene, I-benzo(a)anthracene or chrysene, J-benzo(b)fluoranthene, K-benzo(k)fluoranthene, and L-benzo(a)pyrene. The major peaks in the leachate background in Figure 3 correspond to A-naphthalene, 1and 2-methyl naphthalene (Rt. 8.3 and 8.5 min), D-fluorene, E-phenanthrene, F-anthracene, G-fluoranthene, I-benzo(a)anthracene or chrysene, and L-benzo(a)pyrene. The peak corresponding to anthracene is an interference because there is very little signal that corresponds to anthracene in the chromatogram from the fluroesence detector. When the precleanup extract is analyzed by HPLC, the presence of the late eluting PNAs is obscured by the rising baseline on the fluoresence detector.

In order to more fully understand the complexity of this leachate matrix, final extracts were subsequently analyzed by GC/MS. The extracts obtained correspond to both the neutral extraction procedure as specified in Method 610 and to the basic and acidic extraction procedure specified in Method 625. The complex extracts obtained after neutral extraction showed little difference from the extract obtained using the basic extraction. The neutral extraction procedure gave less emulsion problems than did the basic extraction procedure. Since the matrix was quite complex, phenols were almost quantitatively extracted during the basic extraction. The only phenol fuound in the acidic fraction was 2-fluorophenol, the surrogate standard and it also carried over into the basic fraction.

There was a large difference in the complexity of the precleanup extract and the postcleanup extract. The total ion chromatograms of leachate extracts, both before and after silica gel cleanup are given in Figure 4. Except for dibenzofuran (10) all polar compounds containing oxygen, nitrogen, and phosphorus were removed by the silica gel column cleanup. Only aromatic hydrocarbons appear to be present in the extract after cleanup.

The precleanup leachate extract, was also analyzed by GC/MS using capillary column chromatography to improve the overall resolution and separation for this complex mixture. A summary of the confirmed and tentative identifications of 43 compounds found in the leachate sample using both packed column and capillary column chromatography is given in Table 2. Fourteen additional compounds were identified after using capillary column chromatography; however, there are still 65 additional peaks in the capillary run that defy interpretation and identification. Packed column chromatography of the postcleanup leachate extract gave identifications for some PNA compounds that were not resolved when the precleanup extract was analyzed using capillary column chromatography.

SECTION 4

CONCLUSIONS

Landfill leachates contain a large number of polar and nonpolar materials. Method 610 performs reasonably well for leachate samples containing µg per liter levels of PNA compounds containing two, three or four fused rings. PNA compounds containing five or six fused rings exhibit low recoveries from landfill leachates. Almost all polar interferences are removed using the silica gel chromatography cleanup procedure. Confirmation of identity in the post cleanup extract is easily performed by GC/MS using packed column chromatography.

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SECTION 5

RECOMMENDATIONS

Since these leachate samples exhibit a serious matrix effect of low recovery for PNA compounds containing five and six fused rings, further research must be performed to improve the accuracy of the analytical method for measuring the high molecular weight PNA compounds in landfill leachates.

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TABLE 1

Recovery and Precision of PNAs Spiked into Landfill Leachate Analysis by Method 610

		Spike Level µg/L	Recovery[a] From Leachate % ± RSD	Background[b] In Leachate µg/L	Recovery[c] Reagent Water % = RSD
A	Naphthalene	10.4	115 ± 5	35.3[d]	79 ± 4
B	Acenaphthylene	13.7	85 ± 6	-	80 ± 4
C	Acenaphthene	17.7	94 ± 7	1.9[d]	81 ± 3
D	Fluorene	1.15	117 ± 6	3.41[d]	84 ± 2
E	Phenanthrene	6.31	81 ± 11	5.05[d]	85 ± 2
F	Anthracene	8.57	71 ± 15	-	71 ± 2
G	Fluoranthene	0.26	119 ± 8	0.81[d]	92 ± 7
H	Pyrene	2.35	62 ± 8	0.52[d]	85 ± 7
I	Benzo(a)Anthracene	0.21	59 ± 10	0.19	82 ± 5
J	Benzo(b)Fluoranthene	0.20	32 ± 14	0.03	90 ± 3
K	Benzo(k)Fluoranthene	0.09	29 ± 14	0.01	94 ± 2
L	Benzo(a)Pyrene	0.20	26 ± 12	0.06[d]	67 ± 2
M	Dibenzo(ah)Anthracene	0.50	15 ± 22	-	86 ± 2
N	Benzo(ghi)Perylene	0.51	16 ± 21	-	86 ± 4
O	Indeno(1,2,3-cd)Pyrene	0.14	10 ± 27	-	94 ± 2

[a] six aliquots
[b] one aliquot
[c] three aliquots
[d] confirmed by GC/MS

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TABLE 2

Compounds Identified in Leachate Samples

	Compound	Retention Times Relative to 4,4'-Dibromobiphenyl[a] Packed Column	Capillary Column	Identification[b]
	Tetrachloroethene	--	0.051	T
	Chlorobenzene	--	0.097	T
	Dimethylbenzene	--	0.132	T
	2-Fluorophenol-Surrogate Standard	--	0.142	--
	Cumene	--	0.212	T
	Camphene	--	0.253	T
1	1,2,4-Trimethylbenzene	0.117	0.296	C
2	1,3-Dichlorobenzene	0.184	0.316	C
3	2,3-Dihydro-1H-indene	0.199	0.343	T
4	1,2-Dichlorobenzene	0.216	0.343	C
	4-Methylbenzene amine	--	0.388	T
	Camphor	--	0.398	T
	Tetramethylbenzene	--	0.426	T
	Triethylphosphate	--	0.432	T
5	Naphthalene	0.392	0.483	C
6	t-Butylphenol	0.482	0.567	T
7	2-Methylnaphthalene	0.482	0.571	C
8	1-Methylnaphthalene	0.506	--	C
	2,6-Di-t-Butylbenzoquinone	--	0.690	T
9	Dicyclohexylamine	0.523	0.700	T
10	Dimethylnaphthalene	0.558	0.649	T
11	Dimethylnaphthalene	0.570	--	T
12	Acenaphthene	0.652	0.705	C
13	Dibenzofuran	0.675	0.725	T
14	Octylphenol	0.705	0.776	T
15	Fluroene	0.734	0.767	C
16	Tributylphosphate	0.754	0.801	T
17	N,N-Dimethyl 4-toluenesulfonamide	0.830	--	T
	2(3H)-Benzothiazolone	--	0.824	T
18	Phenanthrene	0.854	0.884	C
19	N-Ethyl-4-toluenesulfonamide	0.874	0.835	T
20	Methyl phenanthrene	0.936	--	T
21	Dibutylphthalate	0.959	0.969	C
	Phenobarbitol	--	0.989	T
22	4,4'-Dibromobiphenyl-Surrogate Standard	1.000	1.000	--
23	Unknown mol. wt. 238	1.015	1.045	T
24	Fluoranthene	1.044	1.058	C
25	Pyrene	1.082	--	C
26	Tetramethylphenanthrene	1.088	1.102	T

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TABLE 2 (Continued)

	Compound	Retention Times Relative to 4,4'-Dibromobiphenyl[a] Packed Column	Capillary Column	Identification[b]
27	N-cyclohexyl 4-toluenesulfonamide	1.111	1.070	T
28	4,4'-(1-methylethylidene)bisphenol	1.140	1.077	T
29	Tributoxyethyl phosphate	1.187	1.173	T
30	Bis(2-ethyhexyl)phthalate	1.225	--	C
31	Dioctyl phthalate	1.263	1.230	C
	Benzo(a)pyrene	--	1.413	C

[a] Ret. time of 4,4'-dibromobiphenyl is 35.4 min on Packed column, and 20.0 min on capillary column.

[b] T - tentative by similarity of mass spectra; C - confirmed identification by retention time and similarity of mass spectra.

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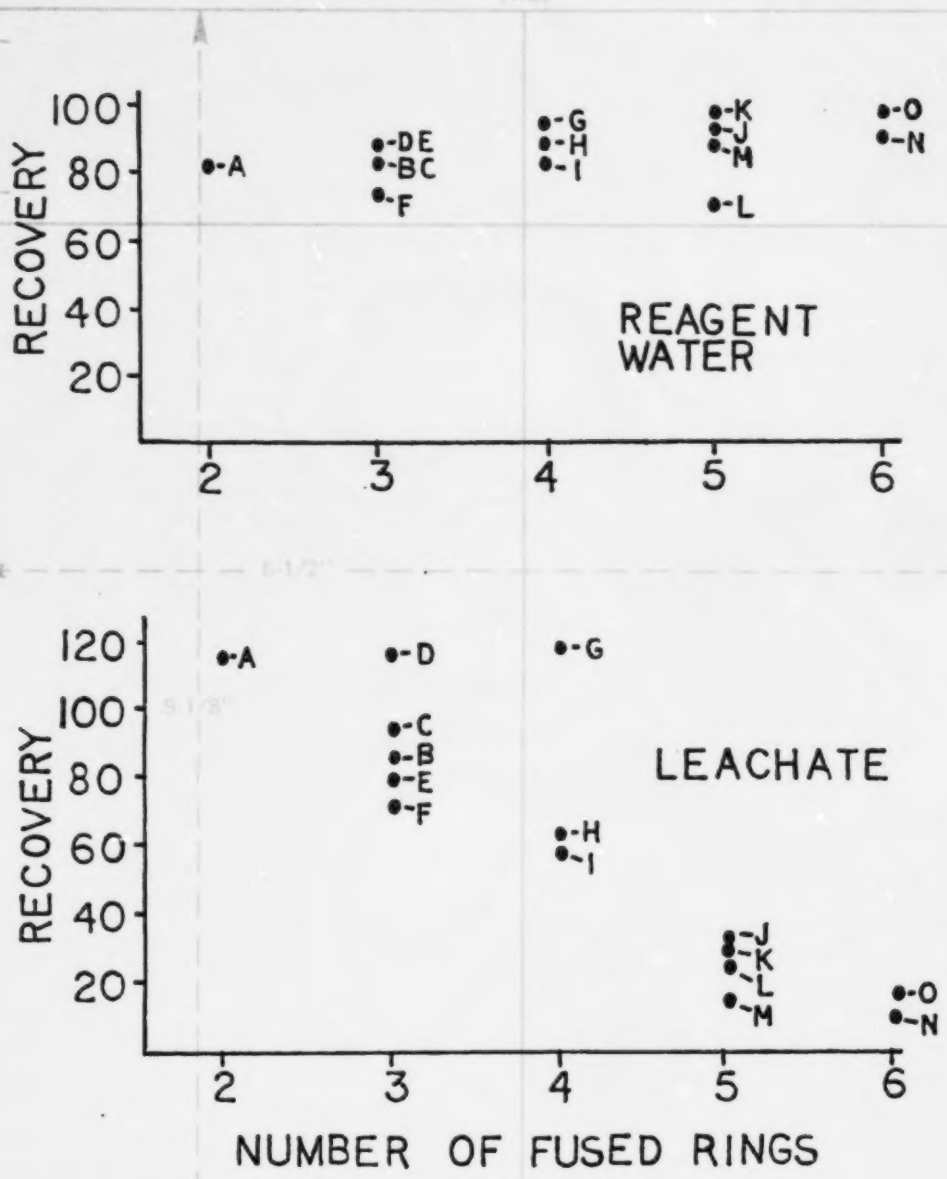

FIGURE 1. Percent recovery versus number of fused rings and matrix.

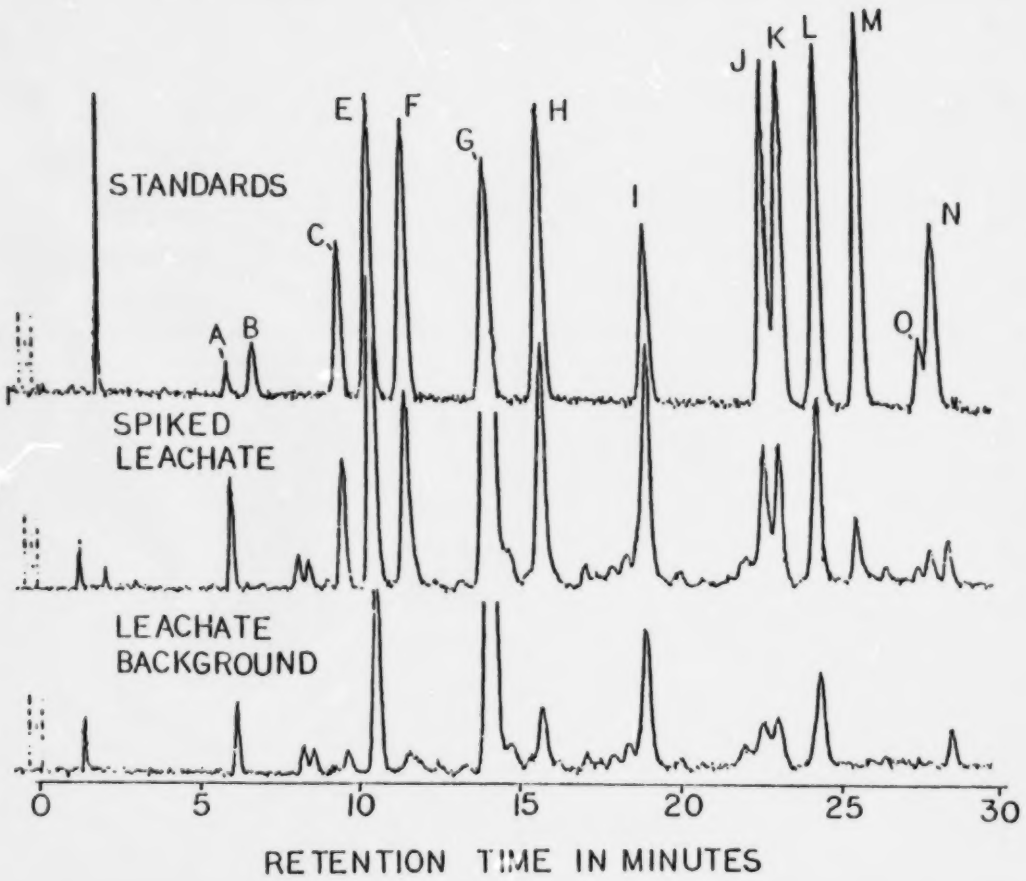

FIGURE 2. HPLC chromatograms of leachate background, spiked leachate, and standards, fluorescence detector.

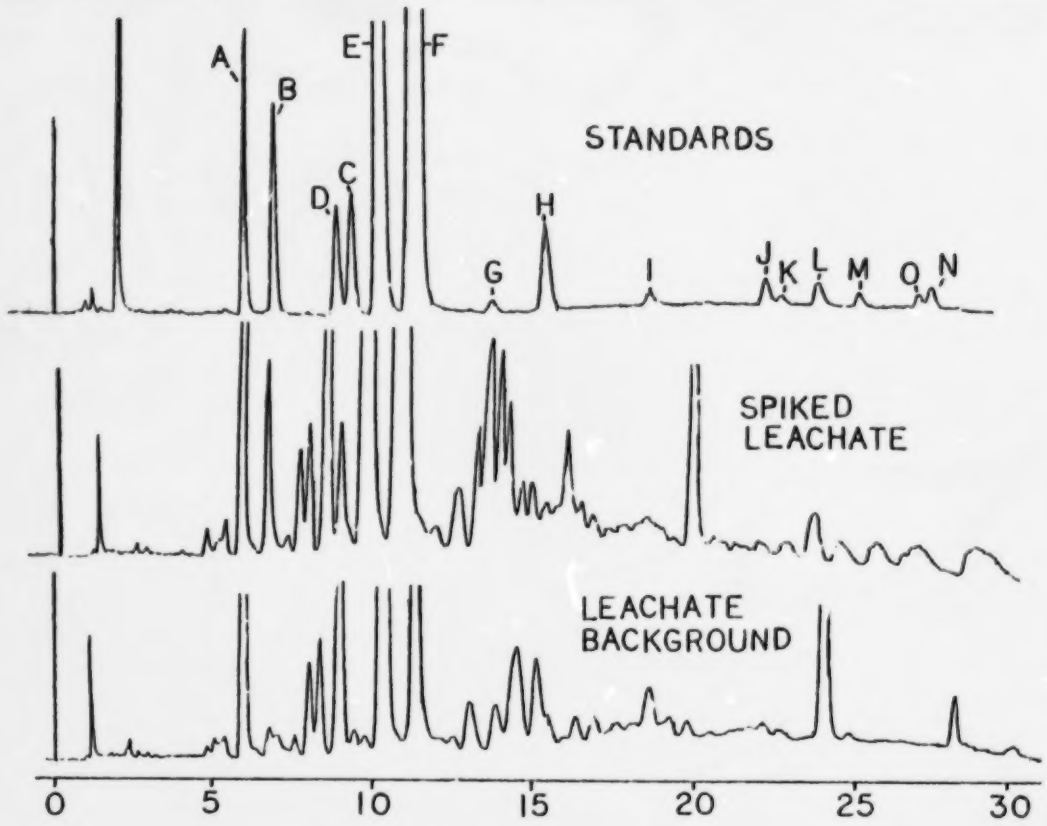

FIGURE 3. HPLC chromatograms of leachate background, spiked leachate and standards, UV detector at 254 nm.

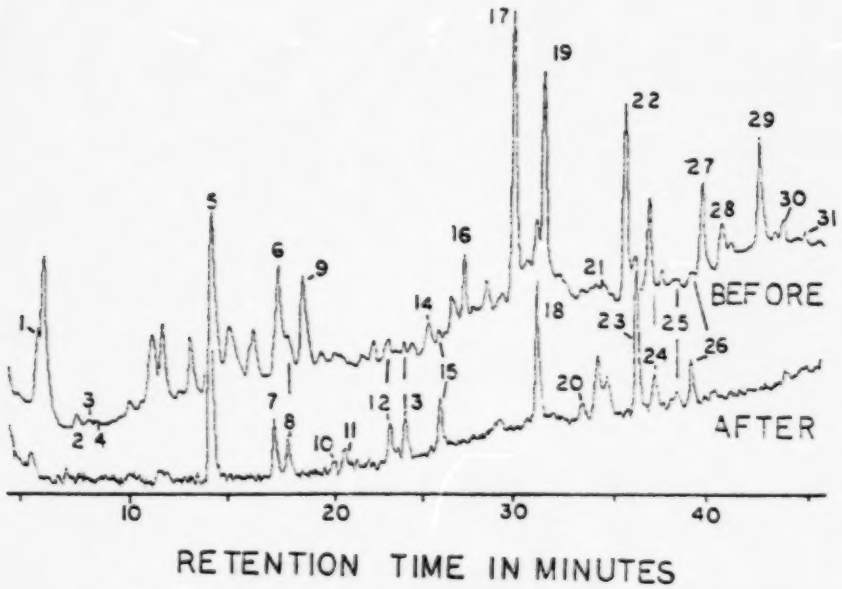

FIGURE 4. Total ion chromatograms of leachate final extracts before and after silica gel column cleanup.